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## CLEANING COMPOSITIONS COMPRISING ALKYL ACID ORTHOPHOSPHATE SURFACTANTS

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This invention relates to improved granular and tableted cleaning compositions comprising, as the surfactant ingredient, certain alkyl acid orthophosphates.

The anionic, non-soap synthetic surface active agents or detergents in prevalent use today are the water soluble salts of organic sulfuric reaction products, such as sodium and potassium alkyl benzene sulfonates, sodium and potassium alkyl glyceryl ether sulfonates, sodium and potassium alkyl sulfonates and sulfates, and the like. Although the anionics are generally available in their acid form, these are converted to the alkali metal, ammonium, or amine salts before admixture with other ingredients in a cleaning composition. The reason for this is that the acid surfactants available heretofore have tended to degrade the condensed phosphate builder, e.g., sodium tripolyphosphate, usually contained in the cleaning formulation.

It is also known that chlorine bleaching agents are not compatible with most if not all of the prior art anionics as well as the nonionic surfactants, whether in acid or salt form.

An object of this invention is to furnish granular and tableted cleaning compositions comprising anionic acid surfactants, and a method of producing the same.

Another object of this invention is to furnish tableted and granular cleaning compositions comprising anionic acid surfactants which are compatible with chlorine bleaching agents.

Other objects will become obvious to those skilled in the art as the description proceeds.

We have now discovered that long chain alkyl acid orthophosphates serve as excellent surface active ingredients which may be included in granular and tableted cleaning compositions, without degrading the other constituents thereof. Thus, a principal feature of the invention is the finding that certain acidic surfactants may be admixed directly with the other ingredients (including condensed phosphates) in cleaning formulations without degrading such other constituents. Another important discovery is that, unlike the prior art anionic sulfuric reaction product surfactants, the alkyl acid orthophosphates of the invention, do not degrade, or are not degraded by, active chlorine-liberating compounds when included in physical admixtures therewith. Accordingly, for all practical purposes, the usual requirement for neutralizing the acid surfactant is obviated.

Suitable alkyl acid orthophosphates which may be used in the cleaning compositions of the invention are the monoalkyl and dialkyl acid orthophosphates and mixtures thereof, in which the total number of carbon atoms per phosphorus atom is from 17 to 23, inclusive. Included among the mixtures which may be used are the  $P_2O_5$ -alcohol reaction mixtures containing both monoalkyl and dialkyl esters, usually about 50% by weight of each. Typical examples of the suitable alkyl acid orthophosphates include didecyl acid orthophosphate, mono di lauryl acid orthophosphate, mono stearyl acid orthophosphate, mono di tridecyl acid orthophosphate, dinonyl acid orthophosphate, 2-ethylhexyl decyl acid orthophosphate, di-n-decyl acid orthophosphate, di-neo decyl acid orthophosphate, metthyl eicosyl acid orthophosphate, di undecyl acid orthophosphate. A preferred class of alkyl acid orthophosphates for use according to the present invention are the com-

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pounds derived from so-called "oxo" or other branched chain alcohols. Thus the alcohols commonly known as iso-alcohols, wherein the carbon chain contains some branching, will form especially desirable alkyl acid orthophosphate. The acid orthophosphates containing less than 17 carbon atoms or more than 23 carbon atoms, while compatible with other detergent ingredients, including chlorine bleaching agents, are far less effective as surfactants than the compounds of the invention.

The cleaning compositions of the present invention include granular and tableted formulations generally useful in industrial or household laundering applications or in suds boosting or hard surface cleaning. Bleaching formulations which contain an active chlorine compound are also within the scope of the invention. Such compositions may contain a large number of well-known ingredients in varying proportions. For example, laundering compositions will normally comprise (1) a builder, (2) a surfactant, and (3) what may be termed "specialized materials." Among the more important of the known builders are the alkali metal meta-, pyro-, and polyphosphates, with the pyro and polyphosphates such as tetrasodium pyrophosphate, sodium tripolyphosphate, and the like being preferred. A typical granular or tableted laundering detergent will normally have between 25% and 80% builder. Laundering compositions according to the invention will usually also contain from 2% to 25% by weight of a surfactant, a significant proportion of which will be an alkyl acid orthophosphate as described hereinbefore. If desired, one or more of the prior art anionic or nonionic surfactants may be included with the alkyl acid orthophosphates, especially where the laundering composition does not contain a chlorine bleaching agent.

The "specialized materials" which are normally contained in a laundering detergent may be inorganic or organic. Among the conventional inorganic materials are fillers, binders (for tableted detergents), and corrosion inhibitors, such as the alkali metal silicates, carbonates, orthophosphates, and sulfates. Some specific examples are trisodium orthophosphate, sodium metasilicate, sodium carbonate, and sodium sulfate. Among the organic materials are included anti-redeposition agents (typically, carboxymethyl cellulose, suds builders, tarnish inhibitors, foam stabilizers, binders (for tableted detergents), foaming agents, fluorescent brightening agents, bacteriostatic agents, bleaching agents, perfumes, coloring matter, preservatives, and the like. The inorganic fillers and corrosion inhibitors in typical laundering compositions may comprise between 0 and 50% by weight of the total compositions whereas the inorganic binders and the organic materials will, together, normally not exceed 15% by weight of the total composition.

Hard surface cleaners and suds boosters may also comprise builders, surfactants, and specialized materials, but usually in different proportions than the laundering compositions. Tableted suds boosters and hard surface cleaners may also require an inorganic or organic binder. As a general rule, suds boosters will comprise predominantly a builder (90-98%), such as sodium tripolyphosphate, and minor amount of surfactant and specialized material (2-10%). Hard surface cleaners typically contain a small amount of builder (10 to 30% by weight), surfactant (1 to 20% by weight), with the remainder being a filler such as sodium sulfate. Any of the above cleaning compositions may also comprise a chlorine bleaching agent.

The alkyl acid orthophosphate surfactants disclosed herein may be used together with bleaching agents in what may be defined as detergent-bleach compositions. These compositions, which may be marketed in granular or tableted form, can include a small proportion of sodium carbonate, sodium silicate, optical brighteners, anti-re-

deposition agents, binders, and the like. To illustrate, a detergent-bleach tablet for home laundering or commercial bleaching operations may comprise between 30% and 80% condensed phosphate or inert filler, 5 to 50% bleach compound, e.g., potassium dichloroisocyanurate, and 1 to 20% of a surfactant, including the alkyl acid orthophosphates of the invention (plus any prior art anionic or non-anionic surfactants desired). Suitable bleaching agents include the inorganic and organic chlorine bleaches such as sodium hypochlorite, potassium dichloroisocyanurate, sodium dichloroisocyanurate, lithium hypochlorite, calcium hypochlorite, trichloroisocyanuric acid, and the various known equivalents thereof.

Due to the acidity of the alkyl acid orthophosphate surfactants, compositions containing these compounds will normally include one or more fairly alkaline inorganic materials, such as sodium carbonate, trisodium phosphate, sodium silicate, or the like, so as to furnish an alkaline pH when dissolved in water for a cleaning application. More specifically, the composition should be formulated to furnish a pH of from about 7 to 12, preferably from 9 to 11, when completely dissolved in a large volume of water. An exception to this requirement is the suds booster type of composition which contains a large amount of builder (usually sodium tripolyphosphate, pH=9.7), with the acid surfactant usually present only in minor proportions, e.g., 1 to 5% trisodium phosphate and sodium carbonate represent preferred alkaline materials for use with the acid orthophosphates since they furnish a drier granular composition during mixing of the ingredients.

The cleaning compositions may also comprise up to approximately 10% by weight of water. For tableted detergents a preferred water content is between 3% and 7% by weight. Water is especially important where tableting the composition since it may provide a binding action.

ing agent is the last component added to the cleaning composition prior to tableting in order to minimize degradation of the bleaching agent by largely absorbing and thus "inactivating" water and/or other incompatible ingredients which would otherwise contact the chlorine.

The following specific examples will further illustrate the above mentioned principles of the invention and in particular the specific results which may be obtained by using the alkyl acid orthophosphates of the present invention in certain detergent formulations. These examples are intended to be illustrative only and no limitations should be implied therefrom.

#### Example 1

To determine the stability of sodium tripolyphosphate in the presence of alkyl acid orthophosphates, various standard detergent formulations were prepared containing these two ingredients. Didecyl acid orthophosphate was selected as the specific acid surfactant to be tested. To serve as a control, similar formulations were prepared containing dodecyl benzene sulfonic acid as the surfactant. The dry ingredients were placed in a Hobart mixer and thoroughly blended prior to addition of liquid ingredients and any water. Finally, the surfactant was added to the other ingredients. These formulations were then placed under storage for six months at room temperature, after which they were analyzed to determine the percentage reversion of the sodium tripolyphosphate to lower phosphates (i.e., ortho, pyro, and metaphosphates). The various formulations and the results obtained therefrom are presented in the following table. (Where the term "carboxymethyl cellulose" is used in the following table and elsewhere herein it is intended to refer to the sodium salt thereof).

TABLE I.—REVERSION OF SODIUM TRIPOLYPHOSPHATE IN THE PRESENCE OF ACID SURFACTANTS—6 MONTHS STORAGE

Ingredients	Formulations (ingredients in percent by weight)					
	1	2	3	4	5	6
Sodium tripolyphosphate.....	50.0	50.0	50.0	50.0	50.0	50.0
Na <sub>2</sub> CO <sub>3</sub> .....	10.0	10.0			10.0	10.0
Trisodium phosphate.....			10.0	10.0		
Na <sub>2</sub> SiO <sub>3</sub> .....	8.0	8.0	8.0	8.0	8.0	8.0
Na <sub>2</sub> SO <sub>4</sub> .....	16.4	21.4	16.4	21.4	21.4	16.4
Carboxymethyl cellulose.....	0.5	0.5	0.5	0.5	0.5	0.5
Optical brightener.....	0.1	0.1	0.1	0.1	0.1	0.1
Water.....	5.0		5.0			5.0
Didecyl acid orthophosphate.....	10.0	10.0	10.0	10.0		
Dodecyl benzene sulfonic acid.....					10.0	10.0
Percent Na <sub>2</sub> P <sub>3</sub> O <sub>10</sub> remaining *at 6 months....	92	91	92	91	87	85

\*Results are comparative only since a commercial grade of tripolyphosphate containing between 92% and 94% Na<sub>2</sub>P<sub>3</sub>O<sub>10</sub> was used.

The granular and tableted cleaning compositions of the invention are prepared by processes well known in this art. For granular compositions the dry ingredients are usually first physically mixed after which the liquid ingredients are sprayed or otherwise applied to an agitated bed of the dry mixture. A homogeneous mixture such as that obtained by spray drying or roll drying an aqueous slurry of the ingredients may also be used. Tableted compositions are produced by compressing granular mixtures of the cleaning ingredients under pressure, usually between 30 and 500 p.s.i. Treatment or curing of the tableted compositions after compression may be employed to enhance the physical characteristics of the tablet. Treatment of tablets by steam or water spray after compression is a common practice in this art, except where the tablets contain appreciable amounts of bleaching agents. Further, as a general practice any chlorine bleach-

Formulations numbered 5 and 6 in the above table produced heat when mixed in the Hobart and the materials caked solid. Upon grinding the material was fairly free flowing, although Formula 6 continued to cake after further standing. Formulas 1 through 4, those containing didecyl acid orthophosphate, did not cake, retained their good flow properties, and no heat was liberated during mixing.

#### Example 2

Granular detergent formulations were prepared according to the procedure described above in Example 1. In one formulation didecyl acid orthophosphate, 95% active, was used as the surfactant while in a control formulation dodecyl benzene sulfonic acid, 95% active, was used for the same purpose. After storage for fourteen days at room temperature paper chromatograms of the detergent formulations were run to determine any differ-

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ences in the amount of reversion of tripolyphosphate. The results are presented in tabular form as follows:

TABLE II.—REVERSION OF SODIUM TRIPOLYPHOSPHATE IN THE PRESENCE OF ACID SURFACTANTS—14 DAYS STORAGE

Ingredients	Formulations (ingredients in parts by weight)	
	1	2
Sodium tripolyphosphate ( $\text{Na}_3\text{P}_3\text{O}_{10}$ ).....	75.0	75.0
$\text{Na}_2\text{CO}_3$ .....	5.5	5.5
$\text{Na}_2\text{SiO}_3$ .....	8.5	8.5
Carboxymethyl cellulose.....	0.5	0.5
Optical brightener.....	0.1	0.1
Didecyl acid orthophosphate.....	9.5	9.5
Dodecyl benzene sulfonic acid.....		
Quantitative evaluation of paper chromatograms, after 14 days*:		
Percent orthophosphate.....	nil	7.2
Percent pyrophosphate.....	6.9	8.9
Percent trimetaphosphate.....	trace	0.7
Percent tripolyphosphate.....	93.0	83.2

\*For a description of this method, see Bernhart, D. N. and Chess W. B., Anal. Chem., Vol. 31, p. 1,926 (June 1959).

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tion, various detergent tablet compositions were prepared. For comparative purposes formulations were also prepared containing a number of popular commercial surfactants. The mixing and tableting procedures were as follows: the granular or powdered sodium tripolyphosphate was first placed in a Hobart mixing bowl after which the other ingredients, namely, sodium sulfate, sodium silicate, CMC, optical brightener, trisodium phosphate, and tetrasodium pyrophosphate were added with mixing. Water, where used, was then added to the pre-mixed ingredients. Mixing was then continued after which the surfactant was added. Finally, potassium dichloroisocyanurate was added with mixing. The mixture was then fed to a Stokes single punch (R-4 model) tableting machine where it was compressed at a pressure between 30 and 300 p.s.i. After tableting, the tablets were allowed to stand at room temperature (about 75° F.) and 70% Relative Humidity for 14 days. At the end of 14 days the tablets were analyzed to determine the amount of available chlorine. The composition of the tablets and the results obtained therefrom are presented in the following table.

TABLE III.—CHLORINE DEGRADATION IN DETERGENT-BLEACH TABLETS CONTAINING VARIOUS SURFACTANTS

Ingredients	Formulations (ingredients in parts by weight)						
	1	2	3	4	5	6	7
Sodium tripolyphosphate (gr.).....	55.0	62.0	62.0	62.0	58.0	55.0	62.0
Sodium tripolyphosphate (powdered).....	7.0				7.0	7.0	
Trisodium phosphate (powdered).....		5.0	5.0				
$\text{Na}_2\text{SO}_4$ .....	7.4	2.3	5.9		7.4	2.4	5.4
$\text{Na}_2\text{SiO}_3$ .....	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Carboxymethyl cellulose.....	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Optical brightener.....	0.1	0.1	0.1	0.1	0.1	0.1	0.1
$\text{H}_2\text{O}$ .....		5.0					5.0
Didecyl acid orthophosphate <sup>1</sup> .....		8.1	5.5				
Sodium didecyl orthophosphate <sup>2</sup> .....	13.0		4.0				
Ultrawet K <sup>3</sup> .....				20.4			
60 K <sup>4</sup> .....					13.0	20.0	
Triton X-100 <sup>5</sup> .....						5.0	10.0
Potassium dichloroisocyanurate.....	9.0	9.0	9.0	9.0	9.0	9.0	9.0
Percent active Cl after 14 days.....	89	82	82	72	52	22	63

<sup>1</sup> Added dry.

<sup>2</sup> Added in 65% aqueous slurry.

<sup>3</sup> Sodium alkyl aryl sulfonate, added dry.

<sup>4</sup> Sodium alkyl aryl sulfonate, added in 60% aqueous slurry.

<sup>5</sup> Non-ionic ethylene oxide adduct of nonyl phenol, added dry.

Formulation number 1 in the above table was found to be clammy after fourteen days, but free flowing. Formulation number 2 solidified and had to be broken up after standing for a few days, after which the material remained free flowing. The analytical data presented in the foregoing table are intended for comparison purposes and are not meant to reflect absolute values or show the total amount of reversion of any of the condensed phosphates. This is due to the fact that a commercial grade of sodium tripolyphosphate containing approximately between 93% and 95% tripolyphosphate as such, (with the remainder substantially all pyrophosphate and metaphosphate) was used in both formulations. Accordingly, the analysis of formulation 1 after 14 days indicates little or no reversion of the tripolyphosphate whereas the tripolyphosphate contained in formulation 2 underwent at least about 10% reversion. Reversion in formulation 2 is indicated both by a decrease in tripolyphosphate content and an increase in pyrophosphate, metaphosphate, and orthophosphate content.

#### Example 3

In order to determine the stability of chlorine bleaching agents in the presence of the acid surfactants of the inven-

From the above table it may be seen that didecyl acid orthophosphate does not effect the availability of a chlorine bleach to the same extent as the prior art anionic or non-anionic surfactants. The bleach was also relatively stable in the presence of the sodium salt of didecyl acid orthophosphate. Formulations numbered 1, 3, 5, and 8 tableted easily while formulations 2 and 4 caused some sticking in the dies. Formulation 6 was extremely tacky and tableted poorly while formulation 7 flaked badly after tableting.

#### Example 4

Granular and tableted detergent formulations similar to those shown in Tables I through III in which the acid surfactant was either mono di lauryl acid orthophosphate, mono stearyl acid orthophosphate, mono di tridecyl acid orthophosphate, dinonyl acid orthophosphate, 2-ethylhexyl decyl acid orthophosphate, di-n-decyl acid orthophosphate, di-neodecyl acid orthophosphate, methyl eicosyl acid orthophosphate, and di undecyl acid orthophosphate were prepared. The condensed phosphates contained in these formulations were found not to be seriously degraded by the acid surfactants nor did the surfactants inactivate chlorine bleaching agents present. These acid surfactants also produced a very high degree of detergency at minimal concentration.

The cleaning compositions described and tested in accordance with Examples 1 through 3 above were evaluated by standard laboratory cleaning procedures to determine their suitability for each disclosed use. To illustrate, standard tests in a TERG-O-TOMETER were accomplished to evaluate the efficiencies of those compositions formulated for laundering operations, while the chlorine-containing formulations were evaluated for bleaching capacity. These tests indicated that all of the compositions comprising the acid orthophosphate surfactants of the invention were equivalent or superior in over-all cleaning power to similar compositions (where such exist) presently manufactured and sold for the same use. Some of the other compositions, e.g., those seriously degraded by the action of the bleach on the surfactant and vice versa; were, of course, inferior and unsuitable for the intended use. The different proportions of surfactants employed in the formulations of Table III generally reflect an attempt to furnish the several compositions with equivalent amounts of detergency (except formulation number 5). Referring to Table III, 8.1 parts by weight of dialkyl acid orthophosphate will yield about the same detergency as 20.4 parts by weight of the sodium alkyl aryl sulfonate in a similar cleaning formulation, and hence such levels were used for comparison purposes.

A further advantage of cleaning compositions containing the alkyl acid orthophosphates is that the alkyl acid orthophosphate is readily biodegradable. Considerable concern has been present in the detergent field in recent years regarding the amount of detergent present in surface waters and subsurface waters. The biodegradability of the alkyl orthophosphates is explained in greater detail in our co-pending application cited above.

The foregoing detailed description is given for clearness of understanding only and no unnecessary limitations are to be derived therefrom, as modification will be obvious to those skilled in the art.

We claim:

1. A cleaning composition consisting essentially of sodium tripolyphosphate and didecyl acid orthophosphate surfactant and furnishing a solution pH between 7 and 12 when completely dissolved in a large volume of water

by the addition of an alkaline material wherein the ratio of condensed phosphate builder to surfactant is from about 98:1 to about 1:2 by weight.

2. A cleaning composition consisting essentially of between 25% and 80% by weight of sodium tripolyphosphate, between 2% and 25% by weight of didecyl acid orthophosphate, and between 0% and 50% by weight of a filler selected from alkali metal silicates, carbonates, orthophosphates, and sulfates, said composition furnishing a solution pH between 9 and 11 when completely dissolved in a large volume of water by the addition of an alkaline material.

3. The cleaning composition of claim 2 in combination with a minor amount of potassium dichloroisocyanurate.

4. A detergent tablet containing the cleaning composition of claim 3.

5. The cleaning composition of claim 2 wherein the filler is selected from trisodium phosphate, sodium metasilicate, sodium carbonate and sodium sulfate.

6. The cleaning composition of claim 2 in combination with from 2% to 10% of a carboxy methyl cellulose anti-redeposition agent.

7. A bleaching composition consisting essentially of a chlorine bleaching agent and didecyl acid orthophosphate surfactant and furnishing a solution pH between 7 and 12 when completely dissolved in a large volume of water, by the addition of an alkaline material, the proportion of said bleaching agent being between 5% and 50% by weight of said composition, the proportion of said acid surfactant being between 1% and 20% by weight of said composition.

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